

Supplementary Information

Impact of atmospheric water-soluble iron on α -pinene-derived SOA formation and transformation in the presence of aqueous droplets

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SI-1: Procedure of Solid-Phase-Extraction

Half of the filter was extracted in 2 mL of 1.25%-NH₃ and shaken for 1 h using a horizontal shaker with 60 rotations per minute. 1.5 mL of the extract were transferred to a brown glass snap lid jar. The extraction procedure was repeated two times resulting in an extraction volume of 3 mL which was subsequently acidified with 60 µL of formic acid (≥99%, VWR, Radnor, USA). The C₁₈ SPE cartridges were conditioned with 1 mL of methanol and 1 mL of 1.25% formic acid. The extract was filtered through a PTFE filter (Minisart SRP4, Sartorius AG, Göttingen, Germany) and added to the SPE cartridges. After washing with 4 mL of 2% formic acid (20 µL formic acid ≥99,0%, Carl Roth, Karlsruhe, Germany in 1 mL HPLC-MS grade H₂O, Carl Roth, Karlsruhe, Germany) the sample was eluted in 800 µL of HPLC-MS grade methanol (HiPerSolv Chromanorm, VWR, Radnor, USA).

According to the protocol the samples were stored in MeOH after the SPE. While Bateman et al. (2008) discovered slow formation of esters by reaction of carboxylic acids, Kourtchev et al. did not observe any differences which could be linked to methylesters of carboxylic acids between boreal forests samples stored in MeOH or acetonitrile.

References

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Table S1: Overview of calculated parameters of experiment 3 describing FS-seed and new formed

experiment	Parameters of 0.1 mM FS-solution			Parameters of particles from nebulized FS-solution				Parameters of new formed particles			Ratio of new formed particles and FS seeds	
	pH	c _{H2O2} [mmol ^{L-1}]	category	A _{salt} [mm ² /m ³]	GMD _{salt} [nm]	TNC _{salt} [# /cm ³]	TMC _{salt} [μg/m ³]	GMD _{mix-salt} [nm]	TNC _{new} [# /m ³]	TMC _{new} [μg/m ³]	Δ GMD _{mix-salt} [nm]	TMC _{new} /A _{salt} [μg/mm ²]
3A-2	≈ 5	0	I	389	34.4	46386	6.0	41,57	80554	12,39	7,14	0,03
3B-2	≈ 5	0	I	584	31.9	86373	7.9	35,75	25879	7,03	3,82	0,012
3A-1	≈ 5	1	II	998	34.9	125740	14.3	39,78	19361	10,19	6,32	0,01
3B-1	≈ 5	1	II	572	30.2	94602	7.3	36,35	23264	5,37	6,15	0,008
3B-2	≈ 5	1	II	982	32.8	137491	13.5	35,4	23048	2,1	2,55	0,002
3A-1	< 3	1	III	882*	*	*	10.6	37,37	52009	31,02	9,21	0,035
3A-2	< 3	0	III	535	28.9	91235	7.0	39,62	76546	40,44	12,62	0,075
3B-2	< 3	0	III	1844	30.7	214138	33.7	31,72	50755	3,02	1,77	0,0016
3A-1	< 3	1	IV	882	28.2	165839	10.6	34,38	58709	25,64	6,22	0,03
3A-2	< 3	1	IV	460	29.0	82344	5.7	39,29	90322	40,92	10,28	0,08
3B-1	< 3	1	IV	806	28.7	147189	9.8	38,98	122432	56,43	10,2	0,07
3B-2	< 3	1	IV	1720	29.9	237284	27.2	33,33	62620	23,69	3,38	0,01

SOA particles

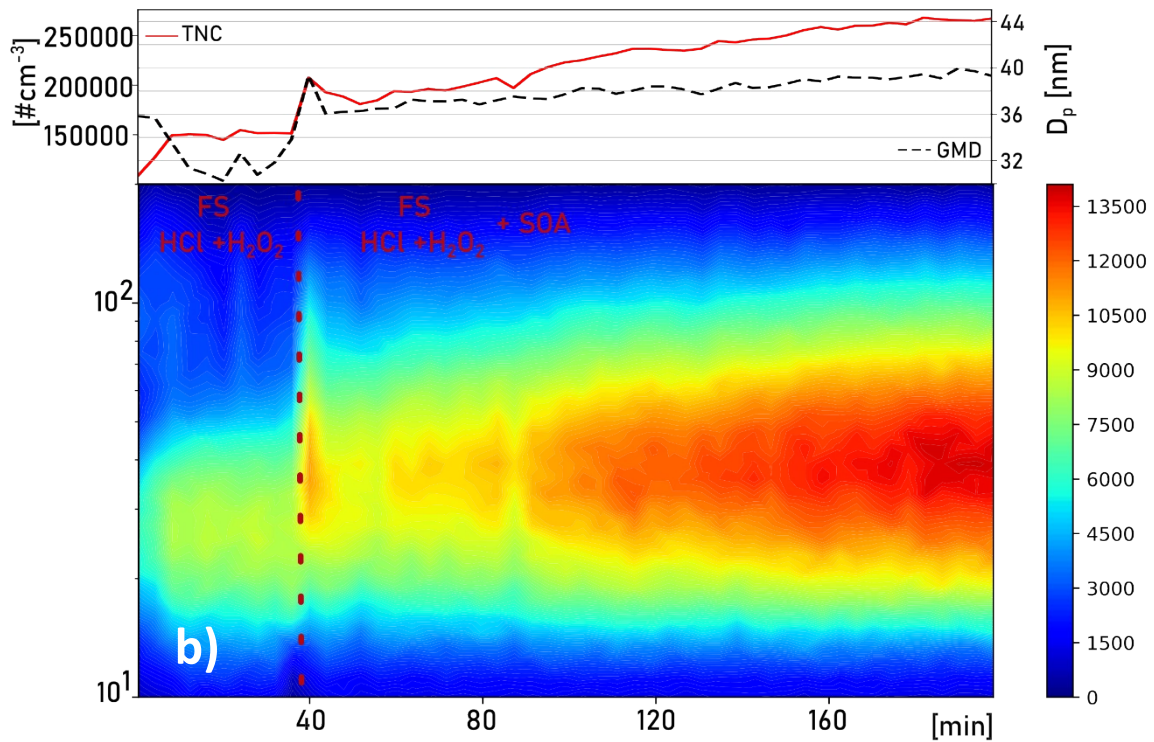
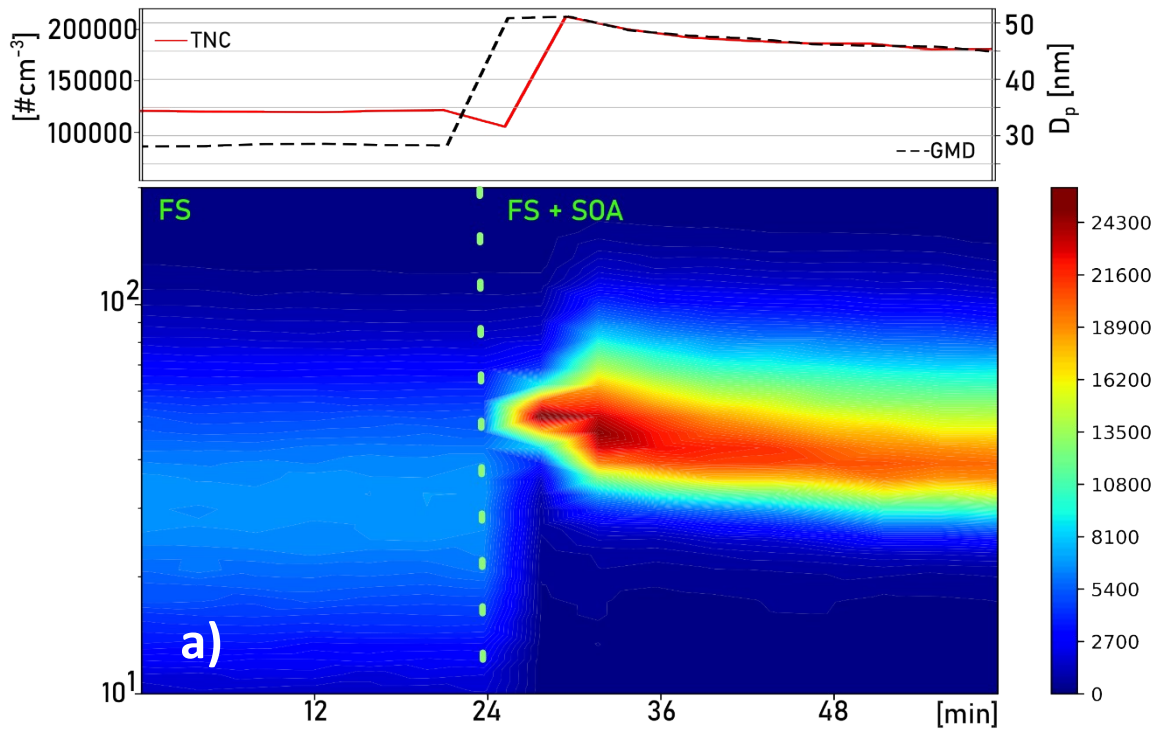


Figure S2: Evolution of particle size distribution over time when initiating SOA formation. Starting times when α -pinene and gaseous ozone were added to the system are marked with the dashed line. **a)** shows quick adjustment of GMD and TNC when only a FS solution is nebulized. **b)** shows that it needed more than 120 min (in this experiment) until stable conditions were reached when nebulizing an acidified solution of category IV.

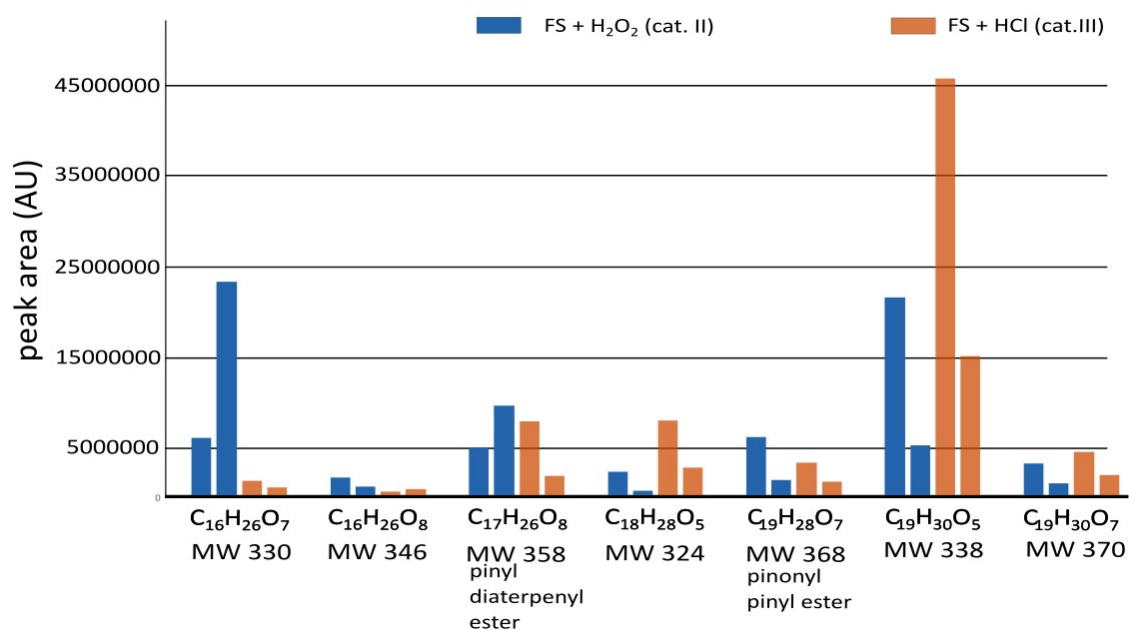


Figure S3: Influence of acidity on dimer abundance in FS samples with pH >3 (blue) or pH <3 (red). The samples are corrected by their differences in organic filter loading. A correction factor was calculated by integrating the total ion count over the range of retention time in which molecules linked to α -pinene-ozonolysis were found.

Table S2: List of m/z values of main oxidation products of targeted analysis

m/z neg. mode	m/z pos mode	Formular	potential substance	Ret. time	Error [Δppm]	RDB	Bidest ref	Fe + H ₂ O ₂ cat. II	Fe + HCl cat. III	Fe+HCl + H ₂ O ₂ cat. IV	reference
	169.122	C ₁₀ H ₁₆ O ₂	pinonaldehyde	8.16	-0.562	2.5	X	X	X	X	
171.066		C ₈ H ₁₂ O ₄	terpenylic acid	7.15	1.035	3.5	X	X	X	X	
185.081		C ₉ H ₁₄ O ₄	pinic acid	6.63	-0.102	3.5	X	X	X	X	
	185.117	C ₁₀ H ₁₆ O ₆	cis-pinonic acid	7.53	-0.56	3.5	X	X	X	X	
187.097		C ₉ H ₁₆ O ₄	diaterpenylic acid acetate	7.54	0.985	2.5	X	X	X	X	
203.055		C ₈ H ₁₂ O ₆	MBTCA	-	-	-	0	0	0	0	
217.108		C ₁₀ H ₁₈ O ₅		6.74	-0.177	2.5	0	X	X	0	Poulain et al., 2022
323.186		C ₁₈ H ₂₈ O ₅		8.42	-1.69	5.5	0	X	X	X	Kenseth et al., 2018
329.16		C ₁₆ H ₂₆ O ₇		7.38	-0.9	5.5	X	X	X	X	
335.185		C ₁₉ H ₂₈ O ₅		6.75	-0.58	5.5	0	0	0	X	Kristensen et al., 2016
337.202		C ₁₉ H ₂₃ O ₅		8.74	-0.47	5.5	X	X	X	X	Kristensen et al., 2016
341.196		C ₁₈ H ₂₃ O ₆		8.17	-0.89	4.5	0	0	X	X	Kenseth et al., 2018
345.155		C ₁₆ H ₂₆ O ₈		8.3	-1.7	4.5	X	X	X	X	Kenseth et al., 2018
353.196		C ₁₉ H ₂₃ O ₆		8.72	-2.44	5.5	0	X	X	X	Kristensen et al., 2016
357.155		C ₁₇ H ₂₆ O ₈	Pinyl diaterpenyl ester	7.8	-0.28	5.5	X	X	X	X	Kristensen et al., 2014
367.175		C ₁₉ H ₂₈ O ₇	Pinonyl-pinyl ester	8.77	-2.52	6.5	X	X	X	X	Kristensen et al., 2014
369.192		C ₁₉ H ₂₃ O ₇		7.55	-0.78	5.5	X	0	X	X	Kenseth et al., 2018
377.145		C ₁₆ H ₂₆ O ₁₀		7.48	-0.98	4.5	X	0	0	0	Kristensen et al., 2016

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